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(54) Title: LIQUID COMPOSITIONS CONTAINING CARBOXYLIC ESTERS (57) Abstract A liquid composition is described which comprises (A) a major amount of at least one fluorine containing hydrocarbon containing one or two carbon atoms; and (B) a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxy groups and characterized by the general formula $R[OC(O)R']_n$.		

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LIQUID COMPOSITIONS CONTAINING CARBOXYLIC
ESTERS

Field of the Invention

This invention relates to liquid compositions comprising a major amount of at least one fluorine-containing hydrocarbon, and a minor amount of at least one lubricant. More particularly, the invention relates to liquid compositions useful as refrigeration liquids.

Background of the Invention

Chlorofluorocarbons, generally referred to in the industry as CFCs, have been widely used as propellants in aerosols, although use in aerosols has been diminishing in recent years because of demands of environmentalists for the reduction if not a complete ban on the use of CFCs because of the detrimental effect of CFCs on the stratosphere's ozone layer. CFCs also have been used because of their unique combination of properties as refrigerants, foam-blowing agents, and specialty solvents within the electronics and aerospace industries. Examples of CFCs which have been utilized for these purposes include CFC-11 which is chlorotrifluoromethane, CFC-12 which is dichlorodifluoromethane, and CFC-113 which is 1,2,2-trifluoro-1,1,2-trichloroethane.

Since 1976, when the aerosol industry began to feel the pressure to reduce if not eliminate the use of CFCs, the aerosol industry has progressively moved

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toward the substitution of hydrocarbon propellants for CFC propellants. The hydrocarbons, such as butane, are readily available and inexpensive, and the quality of the final product generally has been unaffected by the substitution of propellants. However, the problem of finding a safe replacement of CFC refrigerants and foam-blowing agents has been more difficult to solve. Several replacement candidates have been suggested as alternatives to the fully halogenated hydrocarbons, and these include halogenated hydrocarbons containing at least some hydrogen atoms such as HCFC-22 which is difluorochloromethane, HCFC-123 which is 1,1-dichloro-2,2,2-trifluoroethane, HFC-134a which is 1,1,1,2-tetrafluoroethane and HCFC-141b which is 1,1-dichloro-1-fluoroethane.

The ozone depletion potential of these proposed substitutes is significantly less than the ozone depletion potential of the previously used CFCs. The ozone depletion potential is a relative measure of the capability of the material to destroy the ozone layer in the atmosphere. It is a combination of the percentage by weight of chlorine (the atom that attacks the ozone molecule) and the lifetime in the atmosphere. HCFC-22 and HFC-134a generally are recommended as being candidates in refrigerant applications, and HFC-134a is particularly attractive because its ozone depletion potential has been reported as being zero.

In order for any of the replacement materials to be useful as refrigerants, the materials must be compatible with the lubricant utilized in the compressor. The presently used refrigerants such as CFC-12 are readily compatible with mineral lubricating oils which are utilized as the lubricant in air-conditioner compres-

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sors. The above-described refrigerant candidates, however, have different solubility characteristics than the refrigerants presently in use. For example, mineral lubricating oil is incompatible (i.e., insoluble) with HFC-134a. Such incompatibility results in unacceptable compressor life in compression-type refrigeration equipment including refrigerators and air-conditioners including auto, home and industrial air-conditioners. The problem is particularly evident in automotive air-conditioning systems since the compressors are not separately lubricated, and a mixture of refrigerant and lubricant circulates throughout the entire system.

In order to perform as a satisfactory refrigeration liquid, the mixture of refrigerant and lubricant must be compatible and stable over a wide temperature range such as from about 0°C and above 80°C. It is generally desirable for the lubricants to be soluble in the refrigerant at concentrations of about 5 to 15% over a temperature range of from -40°C to 80°C. These temperatures generally correspond to the working temperatures of an automobile air-conditioning compressor. In addition to thermal stability, the refrigeration liquids must have acceptable viscosity characteristics which are retained even at high temperatures, and the refrigeration liquid should not have a detrimental effect on materials used as seals in the compressors.

Compositions comprising a tetrafluoroethane and polyoxyalkylene glycols are discussed in U.S. Patent 4,755,316. The compositions are useful in refrigeration systems. Refrigeration oils are described in U.S. Patents 4,248,726 and 4,267,064 which comprise mixtures of a polyglycol and 0.1 to 10% of glycidyl ether type epoxy compounds, or epoxidized fatty acid monoesters, and

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optionally, epoxidized vegetable oil. The lubricating oils are reported to be useful in refrigerators using a halogen-containing refrigerant such as Freons 11, 12, 13, 22, 113, 114, 500 and 502 (available from DuPont), and in particular with Freon 12 or 22.

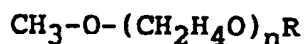
U.S. Patent 4,431,557 describes fluid compositions comprised of a fluoro- and chloro-containing refrigerant, a hydrocarbon oil, and an alkylene oxide additive compound which improves the thermal resistance of the oil in the presence of the refrigerant. Examples of hydrocarbon oils include mineral oil, alkyl benzene oil, dibasic acid ester oil, polyglycols, etc. The composition may contain other additives including load-carrying additives such as phosphorus acid esters, phosphoric acid esters, etc. Examples of fluorocarbon refrigerants include R-11, R-12, R-113, R-114, R-500, etc.

U.S. Patent 4,428,854 describes absorption refrigerant compositions for use in refrigeration systems comprising 1,1,1,2-tetrafluoroethane and an organic solvent capable of dissolving the ethane. Among the solvents disclosed are organic amides, acetonitrile, N-methyl pyrroles, N-methyl pyrrolidine, N-methyl-2-pyrrolidone, nitromethane, various dioxane derivatives, glycol ethers, butyl formate, butyl acetate, diethyl oxalate, diethyl malonate, acetone, methyl ethyl ketone, other ketones and aldehydes, triethyl phosphoric triamide, triethylene phosphate, triethyl phosphate, etc.

Stabilized absorption compositions comprising (a) a halogenated hydrocarbon refrigerant, (b) a liquid absorbent of a polyethylene glycol methyl ether, and (c) at least one stabilizer are described in U.S. Patent 4,454,052. Examples of stabilizers include phosphate

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esters, epoxy compounds, and organotin compounds. The polyethylene glycol methyl ether-type compounds are of the general formula



wherein n is an integer of 1 to 6, and R is H , $\text{CH}_3\text{-}$ or $\text{CH}_3\text{CO-}$. A variety of halogenated hydrocarbons are described including 1,1,-difluoromethane, 1,1,1,2-tetrafluoroethane, etc.

U.S. Patent 4,559,154 relates to absorption heat pumps utilizing as working fluid, a saturated fluorohydrocarbon or fluorohydrocarbon ether having from 3 to 5 carbon atoms. Solvents reported to be useful with such fluorohydrocarbons include ethers such as tetraglyme, amides which can be lactams such as the N -alkyl pyrrolidones, sulfonamides and ureas including cyclic ureas.

Summary of the Invention

A liquid composition is described which comprises

(A) a major amount of at least one fluorine containing hydrocarbon containing one or two carbon atoms; and

(B) a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxy groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R^1 is independently hydrogen, a straight chain low r hydrocarbyl

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group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms provided that at least one R^1 group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2.

Liquid compositions also are described wherein the fluorine-containing hydrocarbons also contain other halogen such as chlorine. The liquid compositions are useful particularly as refrigeration liquids in refrigerators and air-conditioners including auto, home and industrial air-conditioners.

Description of the Preferred Embodiments

Throughout this specification and claims, all parts and percentages are by weight, temperatures are in degrees Celsius, and pressures are at or near atmospheric pressure unless otherwise clearly indicated.

As used in this specification and in the appended claims, the terms "hydrocarbyl" and "hydrocarbylene" denote a group having a carbon atom directly attached to the polar group and having a hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

(1) Hydrocarbon groups; that is, aliphatic, (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Such groups are known to those skilled in the art. Examples include methyl, ethyl, octyl, decyl, octadecyl, cyclohexyl, etc.

(2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which, in

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the context of this invention, do not alter the predominantly hydrocarbon character of the group. Those skilled in the art will be aware of suitable substituents. Examples include halo, hydroxy, alkoxy, etc.

(3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each 10 carbon atoms in the hydrocarbyl group.

Terms such as "alkyl", "alkylene", etc. have meanings analogous to the above with respect to hydrocarbyl and hydrocarbylene.

The term "hydrocarbon-based" also has the same meaning and can be used interchangeably with the term hydrocarbyl when referring to molecular groups having a carbon atom attached directly to the polar group.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, hydrocarbylene, alkylene, alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

When a compound or component is indicated herein as being "soluble", the compound or component is soluble in the liquid compositions of the invention comprising the fluorine-containing hydrocarbon and the lubricant. For example, a compound or component is considered "soluble" so long as it is soluble in the

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liquid compositions, even though it may be insoluble in the fluorine-containing hydrocarbon per se.

(A) Fluorine-Containing Hydrocarbon.

The liquid compositions of the present invention comprise a major amount of at least one fluorine-containing hydrocarbon. That is, the fluorine-containing hydrocarbons contain at least one C-H bond as well as C-F bonds. In addition to these two essential types of bonds, the hydrocarbon also may contain other carbon-halogen bonds such as C-Cl bonds. Because the liquid compositions of the present invention are primarily intended for use as refrigerants, the fluorine-containing hydrocarbon preferably contains one or two carbon atoms, and more preferably two carbon atoms.

As noted above, the fluorine-containing hydrocarbons useful in the liquid compositions of the present invention may contain other halogens such as chlorine. However, in one preferred embodiment, the hydrocarbon contains only carbon, hydrogen and fluorine. These compounds containing only carbon, hydrogen and fluorine are referred to herein as fluorohydrocarbons. The hydrocarbons containing chlorine as well as fluorine and hydrogen are referred to as chlorofluorohydrocarbons. The fluorine-containing hydrocarbons useful in the composition of the present invention are to be distinguished from the fully halogenated hydrocarbons which have been and are being used as propellants, refrigerants and blowing agents such as CFC-11, CFC-12 and CFC-113 which have been described in the background.

Specific examples of the fluorine-containing hydrocarbons useful in the liquid compositions of the present invention, and their reported ozone depletion potentials are shown in the following Table I.

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TABLE I

<u>Compound Designation</u>	<u>Formula</u>	<u>ODP*</u>
HCFC-22	CHClF_2	0.05
HCFC-123	CHCl_2CF_3	<0.05
HCFC-141b	$\text{CH}_3\text{CCl}_2\text{F}$	<0.05
HFC-134a	CH_2FCF_3	0

* Ozone depletion potential as reported in Process Engineering, pp. 33-34, July, 1988.

Examples of other fluorine-containing hydrocarbons which may be useful in the liquid compositions of the present invention include trifluoromethane (HFC-23), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), 1-chloro-1,1-difluoroethane (HCFC-142b), and 1,1,2,2-tetrafluoroethane (HFC-134). In the refrigerant art, the fluorohydrocarbons are often identified merely with the prefix "R" in place of the above letters. For example HFC-23 is R-23, HCFC-124 is R-124, etc. :

In general, fluorine-containing hydrocarbons which are useful as refrigerants are fluoromethanes and fluoroethanes boiling at a relatively low temperature at atmospheric pressure, e.g., below 30°C. Mixtures of fluorine-containing hydrocarbons may be used, and the amount of each fluorohydrocarbon in the mixture may be varied as desired. Examples of fluorohydrocarbon mixtures useful as (A) include: 142(b)/22; 134(a)/23; 22/124/152(a), etc. The useful fluorocarbon refrigerants serve to transfer heat in a refrigeration system by evaporating and absorbing heat at a low temperature and pressure, e.g., at ambient temperature and atmospheric

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pressure, and by releasing heat on condensing at a higher temperature and pressure.

The liquid compositions of the present invention contain a major amount of the fluorine-containing hydrocarbon. More generally, the liquid compositions will comprise from about 50% to about 99% by weight of the fluorine-containing hydrocarbon. In another embodiment, the liquid compositions contain from about 70% to about 99% by weight of the fluorine-containing hydrocarbon.

(B) Soluble Organic Lubricant.

In addition to the fluorine-containing hydrocarbons described above, the liquid compositions of the present invention also contain a minor amount of at least one carboxylic ester of a polyhydroxy compound containing at least two hydroxy groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R¹ is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from about 8 to about 22 carbon atoms provided that at least one R¹ group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic ester-containing hydrocarbyl group, and n is at least 2.

The carboxylic ester lubricants utilized as component (B) in the liquid compositions of the present invention are reaction products of one or more carboxylic acids (or the lower esters thereof such as methyl,

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ethyl, etc.) with polyhydroxy compounds containing at least two hydroxy groups. The polyhydroxy compounds may be represented by the general formula



wherein R is a hydrocarbyl group and n is at least 2. The hydrocarbyl group may contain from 4 to about 20 or more carbon atoms, and the hydrocarbyl group may also contain one or more nitrogen and/or oxygen atoms. The polyhydroxy compounds generally will contain from about 2 to about 10 hydroxy groups and more preferably from about 3 to about 10 hydroxyl groups. The polyhydroxy compound may contain one or more oxyalkylene groups, and, thus, the polyhydroxy compounds include compounds such as polyetherpolyols. The number of carbon atoms and number of hydroxy groups contained in the polyhydroxy compound used to form the carboxylic esters may vary over a wide range, and it is only necessary the carboxylic ester produced with the polyhydroxy compounds be soluble in the fluorine-containing hydrocarbon (A).

The polyhydroxy compounds used in the preparation of the carboxylic esters (I) also may contain one or more nitrogen atoms. For example, the polyhydroxy compound may be an alkanol amine containing from 3 to 6 hydroxy groups. In one preferred embodiment, the polyhydroxy compound is an alkanol amine containing at least two hydroxy groups and more preferably at least three hydroxy groups.

Specific examples of polyhydroxy compounds useful in the present invention include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, glycerol, neopentyl glycol, 1,2-,

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1,3- and 1,4-butanediols, pentaerythritol, dipentaerythritol, tripentaerythritol, triglycerol, trimethylolpropane, sorbitol, hexaglycerol, 2,2,4-trimethyl-1,3-pentanediol, etc. Mixtures of any of the above polyhydroxy compounds can be utilized.

The carboxylic acids utilized in the preparation of the carboxylic esters useful in the liquid compositions of the present invention may be characterized by the following general formula



wherein R^1 is (a), (b), H, a straight chain lower hydrocarbyl group, (c) a branched chain hydrocarbyl group, or (d) a mixture of one or both of (b) and (c) with a straight chain hydrocarbyl group containing from about 8 to about 22 carbon atoms or (e) a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group. Stated otherwise, at least one R^1 group in the ester of Formula I must contain a lower straight chain hydrocarbyl group or a branched chain hydrocarbyl group. The straight chain lower hydrocarbyl group (R^1) contains from 1 to about 7 carbon atoms, and in a preferred embodiment, contains from 1 to about 5 carbon atoms. The branched chain hydrocarbyl group may contain any number of carbon atoms and will generally contain from 4 to about 20 carbon atoms. In one preferred embodiment, the branched chain hydrocarbon group contains from 5 to 20 carbon atoms and in a more preferred embodiment, contains from about 5 to about 14 carbon atoms. The higher molecular weight straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms will contain in some embodiments, from 8 to about 18 carbon atoms, and

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in more preferred embodiments from 8 to about 14 carbon atoms.

In one preferred embodiment, the branched chain hydrocarbyl groups are characterized by the structure



wherein R^2 , R^3 and R^4 are each independently alkyl groups, and at least one of the alkyl groups contains two or more carbon atoms. Such branched chain alkyl groups, when attached to a carboxyl group are referred to in the industry as neo groups and the acids are referred to a neo acid. In one embodiment, R^2 and R^3 are methyl groups and R^4 is an alkyl group containing two or more carbon atoms.

Any of the above hydrocarbyl groups (R^1) may contain one or more carboxy groups or carboxy ester groups such as $-COOR^5$ wherein R^5 is a lower alkyl, hydroxy alkyl or a hydroxy alkyloxy group. Such substituted hydrocarbyl groups are present, for example, when the carboxylic acid R^1COOH (III) is a dicarboxylic acid or a monoester of a dicarboxylic acid. Generally, however, the acid R^1COOH (III) is a monocarboxylic acid since polycarboxylic acids tend to form polymeric products if the reaction conditions and amounts of reactants are not carefully regulated. Mixtures of monocarboxylic acids and minor amounts of dicarboxylic acids or anhydrides are useful in preparing the esters (I).

Examples of carboxylic acids containing a straight chain lower hydrocarbyl group include formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid and heptanoic acid. Examples of carboxylic acids wherein the hydrocarbyl group is a

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branched chain hydrocarbyl group include 2-ethyl-n-butyric acid, 2-hexyldecanoic acid, isostearic acid, 2-methylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-ethylhexanoic acid, neoheptanoic acid, neodecanoic acid, and commercial mixtures of branched chain carboxylic acids such as the mixture identified as Neo 1214 acid from Exxon.

The third type of carboxylic which can be utilized in the preparation of the carboxylic esters are the acids containing a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms. As noted previously, these higher molecular weight straight chain acids can be utilized only in combination with one of the other acids described above since the higher molecular weight straight chain acids are not soluble in the fluorohydrocarbons. Examples of such higher molecular weight straight chain acids include decanoic acid, dodecanoic acid, stearic acid, lauric acid, behenic acid, etc. Examples of dicarboxylic acids include maleic acid, succinic acid, etc.

In another embodiment, the carboxylic acids utilized to prepare the carboxylic esters may comprise a mixture of a major amount of monocarboxylic acids and a minor amount of dicarboxylic acids. The presence of the dicarboxylic acids results in the formation of esters of higher viscosity. The use of mixtures containing larger amounts of dicarboxylic acids should be avoided since the product ester will contain larger amounts of polymeric esters, and such mixtures may be insoluble in the fluorohydrocarbons. An example of such a mixture of 80 parts of neoheptanoic acid and 20 parts of succinic acid.

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The carboxylic esters of Formula I are prepared, as mentioned above, by reacting at least one carboxylic acid with at least one polyhydroxy compound containing at least two hydroxy groups. The formation of esters by the interaction of carboxylic acids and alcohols is acid catalyzed and is a reversible process which can be made to proceed to completion by use of a large amount of alcohol or by removal of the water as it is formed in the reaction. If the ester is formed by transesterification of a lower molecular weight carboxylic ester, the reaction can be forced to completion by removal of the low molecular weight alcohol formed as a result of a transesterification reaction. The esterification reaction can be catalyzed by either organic acids or inorganic acids. Examples of inorganic acids include sulfuric acids and acidified clays. A variety of organic acids can be utilized including paratoluene sulfonic acid, acidic resins such as Amberlyst 15, etc. Organometallic catalysts include, for example, tetraisopropoxy orthotitanate.

The amounts of carboxylic acids and polyhydroxy compounds included in the reaction mixture may be varied depending on the results desired. If it is desired to esterify all of the hydroxyl groups containing in the polyhydroxy compounds, sufficient carboxylic acid should be included in the mixture to react with all of the hydroxyl groups. When mixtures of the alcohols are reacted with a polyhydroxy compound in accordance with the present invention, the carboxylic acids can be reacted sequentially with the polyhydroxy compounds or a mixture of carboxylic acids can be prepared and the mixture reacted with the polyhydroxy compounds. In one preferred embodiment wherein mixtures of acids are utilized,

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the polyhydroxy compound is first reacted with one carboxylic acid, generally, the higher molecular weight branched chain or straight chain carboxylic acid followed by reaction with the straight chain lower hydrocarbyl carboxylic acid. Throughout the specification and claims, it should be understood that the esters also can be formed by reaction of the polyhydroxy compound with the anhydrides of any of the above-described carboxylic acids. For example, esters are easily prepared by reacting the polyhydroxy compounds either with acetic acid or acetic anhydride.

The formation of esters by the reaction of carboxylic acids or anhydrides with the polyhydroxy compounds described above can be effected by heating the acids or anhydrides, the polyhydroxy compounds, and an acid catalyst to an elevated temperature while removing water or low molecular weight alcohols formed in the reaction. Generally, temperatures of from about 75°C to about 200°C or higher are sufficient for the reaction. The reaction is completed when water or low molecular weight alcohol is no longer formed, and such completion is indicated when water or low molecular weight esters can no longer be removed by distillation.

In some instances, it is desired to prepare carboxylic esters wherein not all of the hydroxyl groups have been esterified. Such partial esters can be prepared by the techniques described above and by utilizing amounts of the acid or acids which are insufficient to esterify all of the hydroxyl groups.

The following examples illustrate the preparation of various carboxylic esters which are useful as lubricants (B) in the liquid compositions of the invention.

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Example 1

A mixture of 92.1 parts (1 mole) of glycerol and 316.2 parts of acetic anhydride is prepared and heated to reflux. The reaction is exothermic and continues to reflux at 130°C for about 4.5 hours. Thereafter the reaction mixture is maintained at the reflux temperature by heating for an additional 6 hours. The reaction mixture is stripped by heating while blowing with nitrogen, and filtered with a filter aid. The filtrate is the desired ester.

Example 2

A mixture of 872 parts (6.05 moles) of 2-ethylhexanoic acid, 184 parts (2 moles) of glycerol and 200 parts of toluene is prepared and blown with nitrogen while heating the mixture to about 60°C. Para-toluene sulfonic acid (5 parts) is added to the mixture which is then heated to the reflux temperature. A water/toluene azeotrope distills at about 120°C. A temperature of 125-130°C is maintained for about 8 hours followed by a temperature of 140°C for 2 hours while removing water. The residue is the desired ester.

Example 3

Into a reaction vessel there are charged 600 parts (2.5 moles) of triglycerol and 1428 parts (14 moles) of acetic anhydride. The mixture is heated to reflux in a nitrogen atmosphere and maintained at the reflux temperature (125-130°C) for about 9.5 hours. The reaction mixture is nitrogen stripped at 150°C and 15 mm.Hg. The residue is filtered through a filter aid, and the filtrate is the desired ester.

Example 4

A reaction vessel is charged with 23 parts (0.05 mole) of hexaglycerol and 43.3 parts (0.425 mole)

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of acetic anhydride. The mixture is heated to the reflux temperature (about 139°C) and maintained at this temperature for a total of about 8 hours. The reaction mixture is stripped with nitrogen and then vacuum stripped to 150°C at 15 mm.Hg. The residue is filtered through a filter aid, and the filtrate is the desired ester.

Example 5

A mixture of 364 parts (2 moles) of sorbitol, and 340 parts (2 moles) of a commercial C₈₁₀ straight chain methyl ester (Procter & Gamble), is prepared and heated to 180°C. The mixture is a two-phase system. Para-toluene sulfonic acid (1 part) is added, and the mixture is heated to 150°C whereupon the reaction commences and water and methanol evolve. When the solution becomes homogeneous, 250 parts (2.5 moles) of acetic anhydride are added with stirring. The reaction mixture then is stripped at 150°C and filtered. The filtrate is the desired ester of sorbitol.

Example 6

A mixture of 536 parts (4 moles) of trimethylol propane and 680 parts (4 moles) of a commercial C₈₁₀ straight chain methyl ester is prepared, and 5 parts of tetraisopropoxy orthotitanate are added. The mixture is heated to 200°C with nitrogen blowing. Methanol is distilled from the reaction mixture. When the distillation of methanol is completed by nitrogen blowing, the reaction temperature is lowered to 150°C, and 408 parts (4 moles) of acetic anhydride are added in a slow stream. A water azeotrope begins to evolve when 50 parts of toluene are added. When about 75 parts of a water/acetic acid mixture has been collected, the distillation ceases. Acetic acid (50 parts) is added and additional

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water/acetic acid mixture is collected. The acetic acid addition is repeated with heating until no water can be removed by distillation. The residue is filtered and the filtrate is the desired ester.

Example 7

A mixture of 402 parts (3 moles) of trimethylol propane, 660 parts (3 moles) of a commercial straight chain methyl ester comprising a mixture of about 75% C₁₂ methyl ester and about 25% C₁₄ methyl ester, (CE1270 from Procter & Gamble), and tetraisopropoxy orthotitanate is prepared and heated to 200°C with mild nitrogen blowing. The reaction is allowed to proceed overnight at this temperature, and in 16 hours, 110 parts of methanol is collected. The reaction mixture is cooled to 150°C, and 100 parts of acetic acid and 50 parts of toluene are added followed by the addition of an additional 260 parts of acetic acid. The mixture is heated at about 150°C for several hours yielding the desired ester.

Example 8

A mixture of 408 parts (3 moles) of pentaerythritol and 660 parts (3 moles) of the CE1270 methyl ester used in Example 7 is prepared with 5 parts of tetraisopropyl orthotitanate, and the mixture is heated to 220°C under a nitrogen purge. No reaction occurs. The mixture then is cooled to 130°C, and 250 parts of acetic acid are added. A small amount of para-toluenesulfonic acid is added and the mixture is stirred at about 200°C for 2 days, and 60 parts of methanol are removed. At this time, 450 parts of acetic anhydride are added and the mixture is stirred at 150°C until the acetic acid/water azeotrope no longer evolves. The residue is filtered through a filter aid, and the filtrate is the desired ester of pentaerythritol.

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Example 9

A mixture of 850 parts (6.25 moles) of pentaerythritol, 3250 parts (25 moles) of neoheptanoic acid, and 10 parts of tetraisopropoxy orthotitanate is prepared and heated to 170°C. Water is evolved and removed by distillation. When the evolution of water ceases, 50 parts of acidified clay are added and some additional water is evolved. A total of about 250 parts of water is removed during the reaction. The reaction mixture is cooled to room temperature and 310 parts of acetic anhydride are added to esterify the remaining hydroxyl groups. The desired ester is obtained.

Example 10

A mixture of 544 parts (4 moles) of pentaerythritol, 820 parts (4 moles) of Neo 1214 acid, a commercial acid mixture available from Exxon, 408 parts (4 moles) of acetic anhydride and 50 parts of Amberlyst 15 is prepared and heated to about 120°C whereupon water and acetic acid begin to distill. After about 150 parts of water/acetic acid are collected, the reaction temperature increases to about 200°C. The mixture is maintained at this temperature of several days and stripped. Acetic anhydride is added to esterify any remaining hydroxyl groups. The product is filtered and the filtrate is the desired ester.

Example 11

A mixture of 1088 parts (8 moles) of pentaerythritol, 1360 parts (8 moles) of a commercial methyl ester of an acid mixture comprising about 55% of C₈, 40% of C₁₀ and 4% of C₆ acids ("CE810 Methyl Ester", Procter & Gamble), 816 parts of acetic anhydride and 10 parts of paratoluene sulfonic acid is prepared and heated to reflux. About 500 parts of a volatile material

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are removed. A water azeotrope mixture then distills resulting in the removal of about 90 parts of water. Acetic anhydride (700 parts) is added and the mixture is stirred as a water/acetic acid mixture is removed. The reaction is continued until no more water is evolved and no free hydroxy groups remain (by IR). The reaction product is stripped and filtered.

Example 12

A mixture of 508 parts (2 moles) of dipentaerythritol, 812 parts (8 moles) of acetic anhydride, 10 parts of acidified clay as catalyst and 100 parts of xylene is prepared and heated to 100°C. This temperature is maintained until the solid dipentaerythritol is dissolved. A water/acetic acid azeotrope is collected, and when the rate of evolution diminishes, the reaction mixture is blown with nitrogen. About 100-200 parts of acetic acid are added and the reaction is continued as additional water/acetic acid/xylene azeotrope is collected. When an infrared analysis of the reaction mixture indicates a minimum of free hydroxyl groups, the reaction mixture is stripped and filtered. The filtrate is the desired product which solidifies.

Example 13

A mixture of 320 parts (1.26 moles) of dipentaerythritol, 975 parts (1.25 moles) of neoheptanoic acid and 25 parts of Amberlyst 15 catalyst is prepared and heated to 130°C. At this temperature water evolution is slow, but when the temperature is raised to 150°C, about 65% of the theory water is collected. The last amounts of water are removed by heating to 200°C. The product is a dark viscous liquid.

Example 14

A mixture of 372 parts (1 mole) of tripentaerythritol, 910 parts (7 moles) of neoheptanoic acid and

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30 parts of Amberlyst 15 catalyst is prepared and heated to 110°C as water is removed. The mixture is heated for a total of 48 hours, and unreacted acid is removed by stripping the mixture. The residue is the desired ester.

Example 15

A mixture of 1032 parts (6 moles) of neodecanoic acid, 450 parts (3 moles) of triethylene glycol and 60 parts of Amberlyst 15 is prepared and heated to 130°C. A water azeotrope is evolved and collected. The residue is the desired product.

Example 16

A mixture of 1032 parts (6 moles) of neodecanoic acid and 318 parts (3 moles) of diethylene glycol is prepared and heated to 130°C in the presence of 20 parts of Amberlyst 15. After heating for 24 hours and removing about 90 parts of water, 20 parts of Amberlyst 15 are added and the reaction is conducted for another 24 hours. The reaction is stopped when the theory amount of water is obtained, and the residue is the desired ester.

Example 17

A mixture of 200 parts (2 moles) of succinic anhydride and 62 parts (1 mole) of ethylene glycol is heated to 120°C, and the mixture becomes a liquid. Five parts of acidic clay are added as catalyst, and an exotherm to about 180°C occurs. Isooctanol (260 parts, 2 moles) is added, and the reaction mixture is maintained at 130°C as water is removed. When the reaction mixture becomes cloudy, a small amount of propanol is added and the mixture is stirred at 100°C overnight. The reaction mixture then is filtered to remove traces of oligomers, and the filtrate is the desired ester.

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Example 18

A mixture of 200 parts (2 moles) of succinic anhydride, 62 parts (1 mole) of ethylene glycol and 1 part of paratoluene sulfonic acid is prepared and heated to 80-90°C. At this temperature, the reaction begins and an exotherm to 140°C results. The mixture is stirred at 130-140°C for 15 minutes after 160 parts (2 moles) of 2,2,4-trimethylpentanol are added. Water evolves quickly, and when all of the water is removed, the residue is recovered as the desired product.

Example 19

A mixture of 294 parts (3 moles) of maleic anhydride and 91 parts (1.5 moles) of ethylene glycol is prepared and heated at about 180°C whereupon a strong exotherm occurs and the temperature of the mixture is raised to about 120°C. When the temperature of the mixture cools to about 100°C, 222 parts (3 moles) of n-butyl alcohol and 10 parts of Amberlyst 15 are added. Water begins to evolve and is collected. The reaction mixture is maintained at 120°C until 50 parts of water is collected. The residue is filtered, and the filtrate is the desired product.

Example 20

A mixture of 1072 parts (8 moles) of trimethylolpropane, 2080 parts (16 moles) of neopheptanoic acid and 50 parts of Amberlyst 15 is prepared and heated to about 130°C. A water/acid azeotrope evolves and is removed. When about 250 of the azeotrope has been removed, 584 parts (4 moles) of adipic acid are added and the reaction continues to produce an additional 450 parts of distillate. At this time, 65 parts of trimethylolpropane are added to the mixture and additional water is removed. The residue is filtered and the filtrate is the desired ester.

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The organic lubricants characterized by Formula I preferably contain branched alkyl groups and generally are free of acetylenic and aromatic unsaturation. Some compounds of Formulae I which contain such unsaturation may be insoluble in the fluorine-containing hydrocarbons. The soluble lubricants of this invention also are preferably free of olefinic unsaturation except that some olefinic unsaturation may be present so long as the lubricant is soluble.

The carboxylic esters (I) are soluble in the fluorine-containing hydrocarbons and, in particular, in the fluorohydrocarbons such as 1,1,1,2-tetrafluoroethane. The lubricants are soluble over a wide temperature range and, in particular, at low temperatures. The solubility of the lubricants in fluorohydrocarbons such as 1,1,1,2-tetrafluoroethane at low temperatures is determined in the following manner. The lubricant (0.5 gram) is placed in a thick-walled glass vessel equipped with a removable pressure gauge. The tetrafluoroethane (4.5 grams) is condensed into the cooled (-40°C) glass vessel, and the contents are warmed to the desired temperature and mixed to determine if the lubricant is soluble in the tetrafluoroethane. If soluble, the temperature of the mixture is reduced until a separation and/or precipitate is observed. The results of this solubility test conducted with several examples of the carboxylic ester lubricants of the present invention are summarized in the following Table II.

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TABLE II

<u>Liquid Containing Product of Example</u>	<u>Solubility °C (ppt.)</u>
6	-45
10	-50
11	-40
12	-50
13	-15
15	-30
16	10
17	-25
19	-10

The liquid compositions of the present invention comprise a major amount of a fluorine-containing hydrocarbon and a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester (I). By "major amount" is meant an amount greater than 50% by weight such as 50.5%, 70%, 99%, etc. The term "minor amount" includes amounts less than 50% by weight such as 1%, 5%, 20%, 30% and up to 49.9%. In one embodiment, the liquid compositions of the present invention will comprise from about 70% to about 99% of the fluorine-containing hydrocarbon and from about 1 to about 30% by weight of the lubricant. In other embodiments, the liquid compositions of the present invention may contain from about 5% to about 20% by weight of the lubricant.

The liquid compositions of the present invention are characterized as having improved thermal and chemical stability over a wide temperature range. Other additives, if soluble in the liquid, known to be useful for improving the properties of halogen-containing hydro-

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carbon refrigerants can be included in the liquid compositions of the present invention to improve the characteristics of the liquid as a refrigerant. However, hydrocarbon oils such as mineral oil generally are not included in and are most often excluded from the liquid compositions of the invention, particularly when the fluorine-containing hydrocarbon contains no other halogen.

The additives which may be included in the liquid compositions of the present invention to enhance the performance of the liquids include extreme-pressure and anti-wear agents, oxidation and thermal-stability improvers, corrosion-inhibitors, viscosity-index improvers, pour point and/or floc point depressants, detergents, dispersants, anti-foaming agents, viscosity adjusters, etc. As noted above, these supplementary additives must be soluble in the liquid compositions of the invention. Included among the materials which may be used as extreme-pressure and anti-wear agents are phosphates, phosphate esters, phosphites, thiophosphates such as zinc diorganodithiophosphates, chlorinated waxes, sulfurized fats and olefins, organic lead compounds, fatty acids, molybdenum complexes, borates, halogen-substituted phosphorous compounds, sulfurized Diels Alder adducts, organic sulfides, metal salts of organic acids, etc. Sterically hindered phenols, aromatic amines, dithiophosphates, phosphites, sulfides and metal salts of dithioacids are useful examples of oxidation and thermal stability improvers. Compounds useful as corrosion-inhibitors include organic acids, organic amines, organic phosphates, organic alcohols, metal sulfonates, organic phosphites, etc. VI improvers include polyolefins such as polyesterbutene, polymethac-

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rylate, polyalkyl styrenes, etc. Pour point and floc point depressants include polymethacrylates, ethylene-vinyl acetate copolymers, succinamic acid-olefin copolymers, ethylene-alpha olefin copolymers, etc. Detergents include sulfonates, long-chain alkyl-substituted aromatic sulfonic acids, phosphonates, phenylates, metal salts of alkyl phenols, alkyl phenol-aldehyde condensation products, metal salts of substituted salicylates, etc. Silicone polymers are a well known type of anti-foam agent. Viscosity adjusters are exemplified by polyisobutylene, polymethacrylates, polyalkyl styrenes, naphthenic oils, alkyl benzene oils, polyesters, polyvinyl chloride, polyphosphates, etc.

The liquid compositions of the present invention are particularly useful as refrigerants in various refrigeration systems which are compression-type systems such as refrigerators, freezers, and air-conditioners including automotive, home and industrial air-conditioners. The following examples are illustrative of the liquid compositions of the present invention.

Parts by Wt.

Example A

1,1,1,2-tetrafluoroethane (HCFC-134a)	90
Lubricant of Example 2	10

Example B

1,1,2,2-tetrafluoroethane	85
Lubricant of Example 4	15

Example C

HCFC-134a	95
Lubricant of Example 6	5

Example D

HCFC-134a	80
Product of Example 1	20

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Example E

HCFC-134a	85
Product of Example 4	15

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

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Claims

1. A liquid composition comprising:

(A) a major amount of at least one fluorine-containing hydrocarbon containing 1 or 2 carbon atoms; and

(B) a minor amount of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxy groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R¹ is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 22 carbon atoms provided that at least one R¹ group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, or a carboxylic acid- or carboxylic acid ester-containing hydrocarbyl group, and n is at least 2.

2. The liquid composition of claim 1 wherein fluorine is the only halogen in the fluorine-containing hydrocarbon (A).

3. The liquid composition of claim 1 wherein the fluorine-containing hydrocarbon (A) is 1,1,1,2-tetrafluoroethane.

4. The liquid composition of claim 1 comprising from about 70% to about 99% by weight of the fluorine-containing hydrocarbon (A) and from about 1 to about 30% by weight of the soluble organic lubricant (B).

5. The liquid composition of claim 1 wherein R¹ in Formula I is a branched chain hydrocarbyl group containing from about 4 to about 20 carbons.

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6. The liquid composition of claim 1 wherein n in Formula I is an integer from 2 to about 10.

7. The liquid composition of claim 6 wherein (B) is derived from a polyhydroxy compound containing oxyalkylene groups.

8. The liquid composition of claim 6 wherein (B) is derived from a polyhydroxy compound which is an alkanol amine containing at least 2 hydroxy groups.

9. The liquid composition of claim 1 which is free of alkylene oxide compounds.

10. A liquid composition comprising:

(A) from about 70 to about 99% by weight of at least one fluorine-containing hydrocarbon containing 1 or 2 carbon atoms and wherein fluorine is the only halogen present; and

(B) from about 1 to about 30% by weight of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing at least 2 hydroxy groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R^1 is independently hydrogen, a straight chain lower hydrocarbyl group, a branched chain hydrocarbyl group, or a straight chain hydrocarbyl group containing from 8 to about 18 carbon atoms provided that at least one R^1 group is hydrogen, a lower straight chain hydrocarbyl or a branched chain hydrocarbyl group, and n is at least 2.

11. The liquid composition of claim 10 wherein the fluorine-containing hydrocarbon (A) is 1,1,1,2-tetrafluoroethane.

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12. The liquid composition of claim 10 wherein R^1 is a branched chain alkyl group containing from 4 to about 20 carbon atoms.

13. The liquid composition of claim 10 wherein n is an integer of from 3 to about 10.

14. The liquid composition of claim 10 wherein R is a hydrocarbyl group containing at least one nitrogen or oxygen atom.

15. The liquid composition of claim 10 wherein (B) is a carboxylic ester of pentaerythritol, dipentaerythritol or tripentaerythritol.

16. The liquid composition of claim 10 wherein (B) is a carboxylic ester of an alkanol amine containing at least 3 hydroxy groups.

17. The liquid composition of claim 10 which is free of alkylene oxide compounds.

18. A liquid composition comprising:

(A) from about 70 to about 99% by weight of 1,1,1,2-tetrafluoroethane; and

(B) from about 1 to about 30% by weight of at least one soluble organic lubricant comprising at least one carboxylic ester of a polyhydroxy compound containing from 3 to about 10 hydroxyl groups and characterized by the general formula



wherein R is a hydrocarbyl group, each R^1 is hydrogen, independently a straight chain alkyl group containing from 1 to about 5 carbon atoms, a branched chain alkyl group containing from about 5 to about 20 carbon atoms, or a straight chain alkyl group containing from 8 to about 12 carbon atoms, provided that at least one R^1

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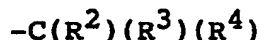
is hydrogen, a straight chain alkyl group containing 1 to about 5 carbon atoms or a branched chain alkyl group containing from about 5 to about 20 carbon atoms, and n is an integer of from 3 to about 10.

19. The liquid composition of claim 18 wherein each R^1 is independently a methyl or ethyl group.

20. The liquid composition of claim 18 wherein each R^1 is a branched chain alkyl group containing from about 5 to about 14 carbon atoms.

21. The liquid composition of claim 18 wherein at least one of the R^1 groups is hydrogen or a methyl or ethyl group and the remaining R^1 groups are branched chain alkyl groups containing from 5 to about 20 carbon atoms.

22. The liquid composition of claim 18 wherein the branched chain alkyl groups are characterized by the structure



wherein R^2 , R^3 and R^4 are each independently alkyl groups and at least one of the alkyl groups contains 2 or more carbon atoms.

23. The liquid composition of claim 22 wherein R^2 and R^3 are methyl groups.

24. The liquid composition of claim 18 wherein the polyhydroxy compound is an alkanol amine containing from 3 to 6 hydroxy groups.

25. The liquid composition of claim 18 wherein the polyhydroxy compound is mono- or dipentaerythritol.

26. The liquid composition of claim 18 which is free of alkylene oxide compounds.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/02069

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 09 K 5/04		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 09 K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	Japanese Patent Office and File Supplier Japs, & JP, A, 56131548 (NIPPON OIL & FATS CO. LTD) 15 October 1981 see the whole abstract --	1,2,10,15,25
X	Japanese Patent Office and File Supplier Japs, & JP, A, 60085478 (TEIJIN MEMORETSUKUSU K.k.) 14 May 1985 see the whole abstract --	1,2,8,15,18, 25
X	Japanese Patent Office and File Supplier Japs, & JP, A, 61181895 (NIPPON OIL & FATS) 14 August 1986 see the whole abstract -- ./.	1,2,10
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
13th July 1990		17. 08. 90
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		M. SOTELO

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	GB, A, 2216541 (ICI) 11 October 1989 see page 2, line 33 - page 3, line 28; claims 1,12 --	1-9,18
Y	EP, A, 0315069 (DAIKIN IND.) 10 May 1989 see page 2, lines 1-40; claims 1-3 --	1-3,7-8
Y	US, A, 4758366 (PAREKH) 19 July 1988 see column 1, line 50 - column 3, line 15; claims 1,3,16 -----	1-3,7-8

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9002069
SA 36425

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 10/08/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2216541	11-10-89	None	
EP-A- 0315069	10-05-89	JP-A- 1118590 US-A- 4923626	11-05-89 08-05-90
US-A- 4758366	19-07-88	JP-A- 61211391	19-09-86